SURFACE DYNAMICS OF CO LAYERS ADSORBED OF Pt(111) MICROFACETS: *IN SITU* TIME-RESOLVED SECOND HARMONIC GENERATION STUDIES

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INTRODUCTION

Recent advances in ultrafast laser pulse technology have opened new prospects for studying fundamental aspects of the kinetics of chemical reactions with unprecedented time resolution.[1] Interest in our laboratory has been focused recently on the implementation of laser-based spectroscopic methods for monitoring dynamics of surface events at solid-liquid interfaces with emphasis on surface reconstruction and oxidation-reduction of adsorbed species. One of such strategies involves application of a fast electrical perturbation, such as a potential or a current step, while following the time evolution of the interface using a fast optical probe. Although conceptually simple, realization of such conditions requires, in practice, careful attention to cell design and instrumentation, as the response, even for ideally polarizable interfaces, is governed by the size of the electrode and the electrolyte resistance.[2] This work describes experiments aimed at monitoring the dynamics of the electrochemically induced CO(2x2) $\longleftrightarrow$ CO($\sqrt{19}\times\sqrt{19}$) R23.4^o transition on Pt(111) microfacets (10 μm diameter) formed spontaneously on the surface of single crystal Pt microspheres (0.75 mm diameter) using *in situ* time-resolved second harmonic generation (SHG) as an interfacial specific probe. Based on the results obtained, the kinetics for the CO(2x2) $\rightarrow$ ($\sqrt{19}\times\sqrt{19}$) R23.4^o transition are more than three orders of magnitude slower than for the reverse process.

EXPERIMENTAL

Various aspects of the preparation of Pt(111) facetted single crystal Pt microspheres and the system for SHG measurements have been reported elsewhere and will not be repeated here.[3] All experiments were carried out in a 1x1cm quartz fluorimetric cuvette with five transparent windows with the single crystal Pt microsphere working electrode mounted on the Teflon cap of the cuvette. A Pt gauze placed at the bottom of the cuvette was used as counter electrode and a reversible hydrogen electrode in the same solution (RHE) connected to the cuvette through a thin Teflon tubing was used as a reference electrode. An EG&G Model 175 Universal Programmer and Model 173 Potentiostat/Galvanostat was used to scan or step the input potential to the potentiostat and to trigger initialization of the data acquisition system. All experiments were performed at room temperature in 0.10 M $HClO_4$ solutions purged using UHP Ar.

RESULTS AND DISCUSSION

Fig. 1 shows a plot of the intensity of the SHG signal, $I_{pp}(2\omega)$, where the subscript pp refers to p-input and p-output polarization, for a Pt(111) microfacet formed on a single crystal microsphere, ca. 0.75 mm diameter, recorded *in situ* in a CO-saturated aqueous solution 0.1 M $HClO_4$ during a linear potential scan in the region $0.0 < E < 1.0$ V vs RHE at a rate of 50 mV/s. As indicated therein, a sizable increase in $I_{pp}(2\omega)$ was observed as the potential was scanned in the positive direction beyond 0.8 V following polarization of the electrode at +0.10 V vs RHE for ca. 1 h. This phenomenon has been attributed by Akemann et al.[4,5] to the reconstruction of the adsorbed CO superlattice on Pt(111), from a (2x2) at low potentials to a ($\sqrt{19}$ x ($\sqrt{19}$)R23.4^o at high potentials, where CO occupies on-top and two-fold bridge sites.[6] It may be noted that in our measurements the potential was scanned at 20 mV/s, as opposed to stepped in sequence as in the latter work. This factor may explain the much higher potential at which the onset of this reversible transition was observed. Nevertheless, the relative increase in $I_{pp}(2\omega)$, ca. 50%, agrees very well with the data of Akemann et al. cited above. Evidence that the Pt(111) facet was well oriented was obtained from $I_{pp}(2\omega)$ vs potential data collected *in situ* for the same facet in the absence of CO in solution. As shown in the insert, Fig. 1, $I_{pp}(2\omega)$ was found to be proportional to the applied potential over the range 0.1 to 0.6 V with a slope virtually independent of the direction of the scan in agreement with the behavior described by Corn and coworkers for this specific Pt low index face.[7,8]

Fig. 2 shows a plot of $I_{pp}(2\omega)$ vs time obtained while stepping the potential between 0.043 and 913 mV which represents a cumulative average of ca. 500,000 individual steps. As can be clearly discerned, the CO(2x2) $\rightarrow$ ($\sqrt{19}\times\sqrt{19}$) R23.4^o is significantly slower than the reverse transformation for which the time constant is smaller than the response time of the potentiostat. Efforts are now underway to implement a charge injection approach to ovecome these time limitations.

ACKNOWLEDGEMENTS

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REFERENCES

(1)Zewail, A. H. *J Phys Chem A* **2000**, *104*, 5660-5694.
(2)Robinson, R. S.; McCreery, R. L. *J. Electroanal. Chem* **1985**, *182*, 61-72.
(3) Scherson, D.A. 199th ECS Meeting, Washington DC Abstract #356, Spring 2001
(4)Akemann, W.; Friedrich, K. A.; Linke, U.; Stimming,U. *Surface Science* **1998**, *404*, 571-575.
(5) Akemann, W.; Friedrich, K. A.; Stimming, U. *J. Chem. Phys.* **2000**, *113*, 6864-6874.
(6) Villegas, I.; Weaver, M. J. *J. Chem. Phys.* **1994**, *101*, 1648-1660
(7) Lynch, M. L.; Barner, B. J.; Corn, R. M. *J.Electroanal. Chem.* **1991**, *300*, 447-465.
(8) Lynch, M. L.; Corn, R. M. *J. Phys. Chem.* **1990**, *94*, 4382-4385.

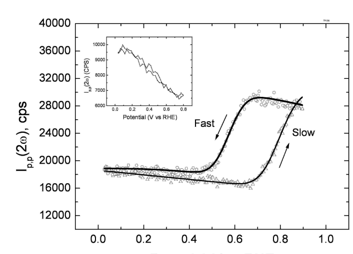

Fig.1 Plot of SHG signal, $I_{pp}(2\omega)$ versus electrode potential for CO saturated 0.1 M hydrochloric acid. Insert shows the same experiment without CO.

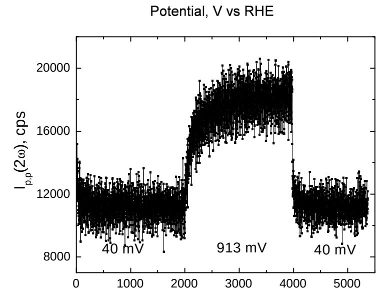

Fig.2 Plot of SHG signal for CO saturated 0.1 M hydrochloric acid when electrode potential is stepped from 43 to 913 mV back to 43 mV vs RHE.